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MICROSTRUCTURAL AND CORROSION STUDIES BY IMMERSION IN 3.5wt % NaCl ENVIRONMENT ON Mg-6Al-1Zn-XCa ALLOY WITH Ca ADDITION AND AGED AT DIFFERENT TEMPERATURES

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ABSTRACT

The effect of aging at different temperatures of 180ºC, 200ºC, 220ºC, and 240º C with various level of calcium (X=0.5, 1, 1.5, 2%) addition on Mg-6Al-1Zn-XCa alloy were investigated in 3.5Wt.% NaCl solution. The specimen was subjected to immersion testing in 3.5Wt.% NaCl, and the resulted surface were analyzed to study the corrosion behaviour and its surface topography by optical microscopy (OM), scanning electron microscopy (SEM), energy dispersed spectroscopy (EDS) and X-ray diffraction (XRD) techniques. The result shows that corrosion attack occurred predominantly on ß phase and the α phase exhibit relatively minor corrosion. In addition to that the increased aging temperature coarsens the intermetallic as well as α- Mg grains, which shows adverse effect to corrosion resistances and the best result were obtained at composition of 0.5wt.% Ca aged at 200°C.

KEYWORDS: Microstructural and Corrosion, 3.5Wt.% NaCl & X-Ray Diffraction

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Original Article

1. INTRODUCTION

The need for lightweight materials in various industries, especially in automobile and aerospace applications has shows significant increase due to the advantage of fuel and great energy saving and utilization [25-26]. And, among the lightweight materials, Magnesium alloys are one of these light weight material, having great chemical stability, machinability and significant high strength to weight ratio [2]. However, their low level of mechanical properties and poor corrosion resistance in chloride environments limits their wider applications [3]. However, it was found that small addition of Ca to a magnesium alloy shows significant increase its strength and corrosion resistance [4-8] in chloride environment. At present, the most widely used magnesium alloys are AZ series materials, and the Corrosion Behavior of magnesium alloy depends on (i) the composition of the Alpha- Mg matrix, (ii) the composition of the other Phases and (iii) its distribution in the matrix[9-14].

Immersion testing is one of the simplest and effective method to study the corrosion behaviour, which was used in this study and the testing procedure been followed is compliance with ASTM G1-72 [15-16]. Based on the literatures the properties of PH, Mg alloys are depending on the precipitates and its distribution in the matrix [17-21]. And, this study is focused on understanding the ageing phenomena with different temperatures and effect of Ca addition to its corrosion behaviour.

2. EXPERIMENTAL PROCEDURE

2.1 Casting

The melting of pure Mg (93wt.%), Al (6wt.%) and Zn(1wt.%) was carried out in stir casting furnace of capacity 1Kg, once the melt was completely in liquid state, Mg-Ca master alloy was added at 720°C, and left 0.5Hrs for reaction and stirred the pool to make uniform melt, subsequently at 650^{o}C of the melt, the gas mixture of 99 % Ar +1% $SF_6$was passed into the crucible at flow rate of 0.25m^3/hr to prevent the unwanted atmospheric contamination to the melt. Then, the melt was poured in to the pre-heated (250°C) metallic mold. The chemical compositions of the experimental alloys are listed in table 1.

Table 1: Chemical Analysis of Experimental Alloy (Mass Fraction, %)

Experimental Alloy	Al	Zn	Ca	Mn	Be	Fe	Cu	Si	Ni	Mg
AZ61	5.78	0.923	-	0.142	0.00067	0.0148	0.004	0.0607	0.0042	Bal.
AZ61+0.5Ca	5.95	0.887	0.40	0.165	0.00052	0.0099	0.004	0.0549	0.0017	Bal.
AZ61+1.0Ca	5.67	0.828	0.8 8	0.173	0.00046	0.0125	0.004	0.0513	0.0017	Bal.
AZ61+1.5Ca	5.67	0.828	1.33	0.173	0.00046	0.0125	0.004	0.0513	0.0017	Bal.
AZ61+2.0Ca	5.33	0.839	1.92	0.172	0.00027	0.013	0.004	0.0503	0.0032	Bal.

2.2. Sample Preparation

The sample for the microstructural analysis, has been prepared from the cylindrical shaped casting, mounted and subsequently polished for the microstructural analysis.

2.3. Immersion Testing

The testing is performed as per ASTM G1-72 and the solution (corrosion environment) of 3.5wt%Nacl been prepared using analytical reagent and distilled water. The specimen shall be immersed completely in to the solution for at least 72 hours, continuously maintained at room temperature

2.4. Evaluation of Corrosion Rate

The corrosion rate was carefully studied by weight loss method as per ASTM G1-72. After the exposure, the specimens were removed from the bath, rinsed with distilled water, dried using compressed air, dried in a desiccator for 1-2 days and weighted to determine the sample weight with corrosion products. [27]

The calculation was performed based on the following formula

$$\Delta W_{cp} = \{(W_{acp} - W_b)[mg]\}/(\text{specimen area }[cm^2])/(\text{exposure time }[d]) \quad (1)$$

Where

ΔW_{cp} – Weight Change rate (with corrosion products)

W_{acp} – Sample weight after the test with corrosion

W_b – products Sample weight before the test

For the Mg alloy corroded specimens, the corrosion products on the surface of the corroded samples were removed by immersing in chromic acid solution of200g/L CrO_3 + 10g/L $AgNO_3$ at room temperature for 5-10 min, and then the sample was washed with distilled water, dried with warm compressed air, and further dried in a desiccators for 1-2

days. Then, the calculation of corrosion rate was determined using the following formula.

$$\Delta W_m = \{(W_b - W_{am})[mg]\}/(\text{specimen area } [cm^2])/(\text{exposure time}[d]) \text{ [15-16]} \qquad (2)$$

Where,

ΔW_m - Weight change rate

W_{am} - With no corrosion products

3. RESULTS AND DISCUSSIONS

3.1. Microstructure Analysis

3.1.1. Effect of Calcium Addition on the Microstructure

The microstructural analysis has been performed in optical microscope DIC lieca model no of capacity ranging from 10X to 1000X magnification. And, the micrographs are presented in the Figure 1.

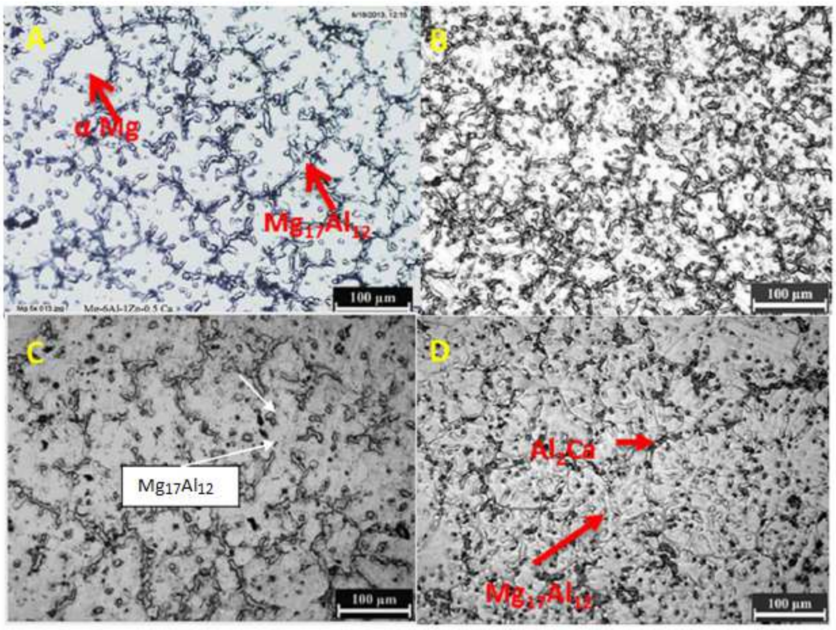
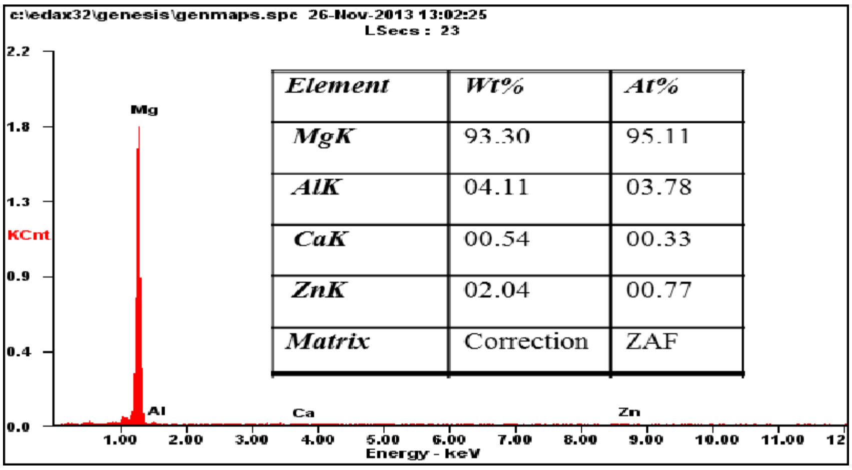


Figure 1: Effect of Calcium Addition on the Microstructure of Alloy AZ61 (a) 0.5% Ca (b) 1.0% Ca (c) 1.5% Ca (d) 2.0% Ca [Etchant 2%Nitol]

Figure.1 shows the effect of Ca addition on the microstructure of AZ61. It is evident that the Ca addition refines α grain size, which enhances the mechanical properties [Figure]. This phenomenon explains that the addition of Ca generates the heterogeneous nucleation of Al_2Ca and it restricts the growth of α grain size. In addition to that the beta ($Mg_{17}Al_{12)}$ grain size also decrease with increasing Ca content, which reduces/replaces Al_2Ca intermetallic in the matrix, which lead to improve the corrosion resistance. With the addition of Ca, the $Mg_{17}Al_{12}$-Mg co-operative eutectic has a reduced quantity or disappears and a new Al_2Ca phase (light gray, also identified by EDS) is formed.



Element	Wt%	At%
MgK	93.30	95.11
AlK	04.11	03.78
CaK	00.54	00.33
ZnK	02.04	00.77
Matrix	Correction	ZAF

Figure 2

3.1.2. Effect of Aging Temperature on the Microstructure

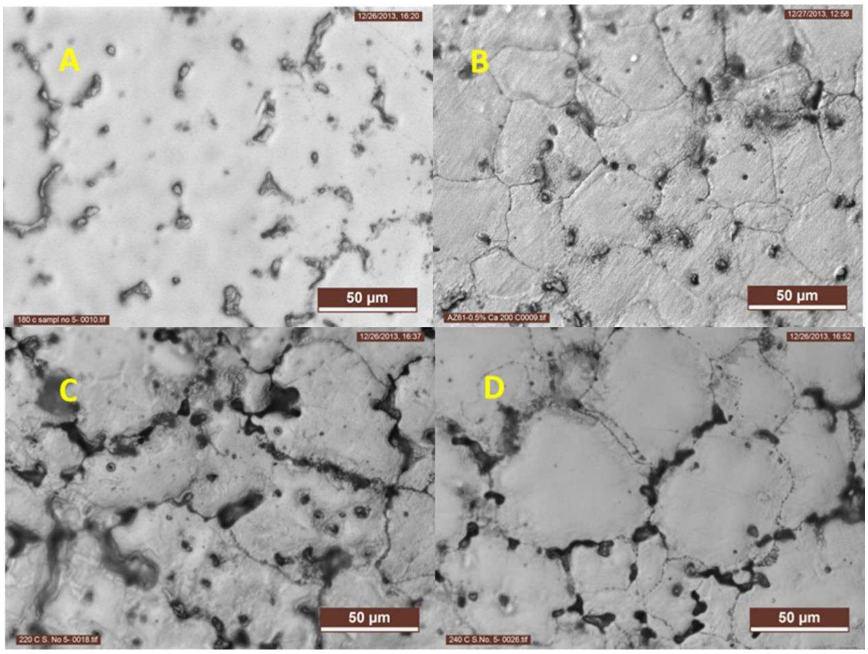


Figure 3: Effect of Aging Temperature on the Microstructure AZ61+0.5Ca Addition Aged at 16 hrs. (a) 180° C (b) 200° C (c) 220° C (d) 240° C

The all 4 combinations listed in Figure 1 were experimented to study structural changes at different level of aging temperature, and the results shows that, the alloy of AZ61+0.5Ca gives better results compare to all other alloy combination, which has been presented in Figure 3, an selected for further investigation.

Based on the evaluation of the micrographs presented in Figure 2,(A,B,C,D), The specimen aged at 200°C shows refined grains and fine and uniform distribution of Al_2Ca along the α grain boundary.

3.3. Microstructure at Various Stages of Aging

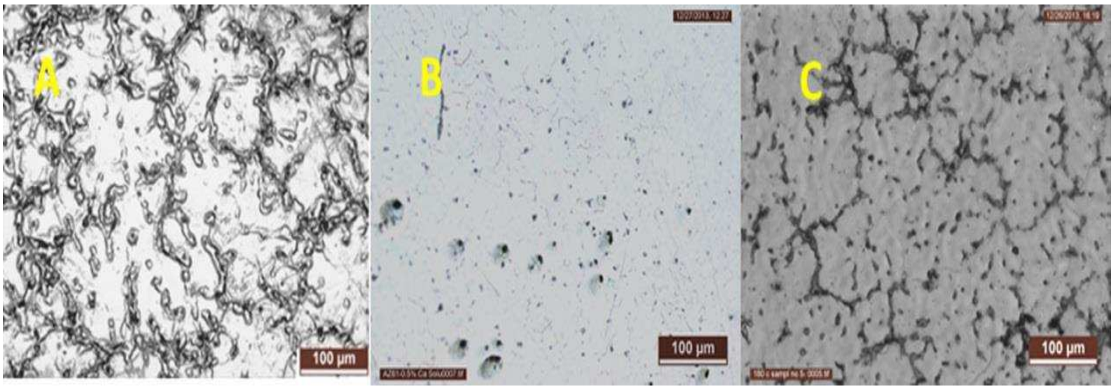


Figure 4: Microstructure of AZ61-0.5Ca-Mg Alloy during Aging (a) without Aging (b) Solutionized at 420°C (c) Aged at 200°C for 16hrs

At Solutionized condition, the micrograph shows complete dissolution of β ($Mg_{17}Al_{12}$) phase, and subsequent ageing for 16 hrs followed by air-cooling. The resulted microstructure (Figure 4.c) shows the nucleation of β ($Mg_{17}Al_{12}$), which enhances the mechanical properties [Figure-Hardness] and the heterogeneous nucleation of Al_2Ca intermetallic in the matrix, which significantly improves the corrosion resistance.

3.2. XRD Analysis

The X-ray Diffraction (XRD) analysis was performed to identify the phases that formed during the aging process.

Figure 5. Shows the XRD analysis for Base AZ61 material (without Ca addition) andAZ61+0.5Ca with and without aging. And, the result clearly shows that the presence of Al2Ca in AZ61+0.5Ca added and aged at 200°C specimen.

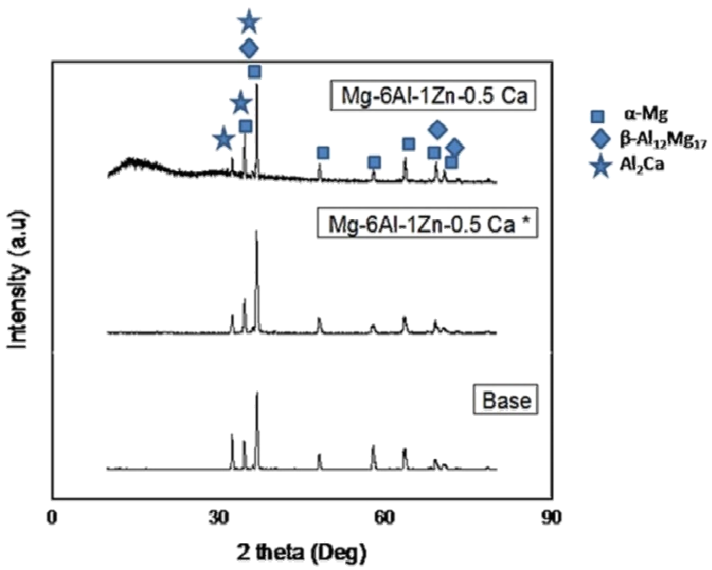


Figure 5: XRD Analysis on Calcium Added Sample and AZ61 Base, * Indicate Specimen without Aging

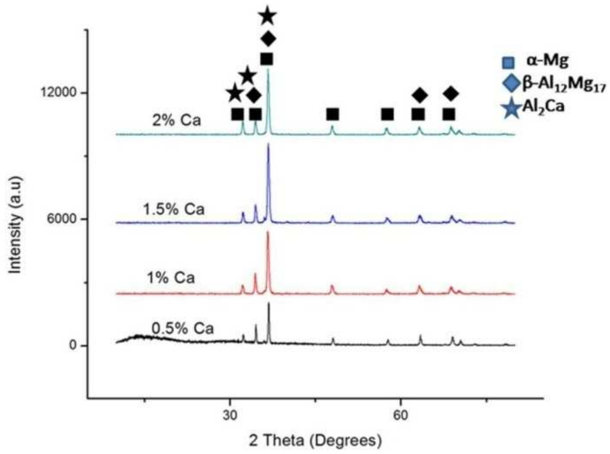


Figure 6: Effect of Calcium on the XRD Result (a) 0.5% Ca (b) 1.0% Ca (c) 1.5% Ca (d) 2.0% Ca

3.3 SEM-EDAX

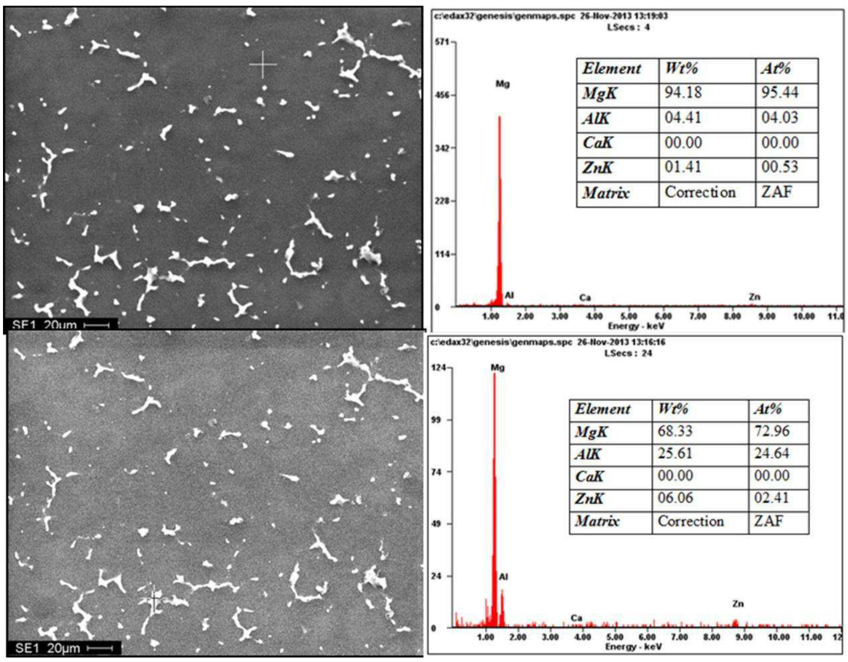


Figure 7: Micro Region & Result of SEM-EDAX Analysis of Specimen AZ61+ 0.5Wt % Ca (As Cast Condition)

Figure 7 shows, the EDAX –SEM analysis which confirms the chemical constituents of the microstructures, the matrix is α phase (at top in Figure 7.) and the chemistry of the β phase (the white precipitates refer bottom Figure 7).

Microhardness Study

Microhardness been performed using MATSUZUWA model MMT-X7 with diamond pyramid indentor and 0.5Kg load, 15s dwell time, and the study was done to analyze the hardness variation with change in aging temperature with different Ca percentage i.e. 0.5,1.0,1.5 and 2.0 Wt.%. The results shows that, increase in aging temperatures increases the hardness, and also increase in Ca addition increases the hardness and then subsequent decrease in hardness, this phenomena is observed same in aging temperatures of 180,200 and 220 °C except 240 °C. The specimen aged at 240°C

shows peak hardness at 1% Ca and then gradually decreases upon subsequenceincrease of Ca to 1.5 and 2%. The direct proportionality for aging temperature/Ca addition to hardness is due to the increasing chances of fine precipitates Al_2Ca.

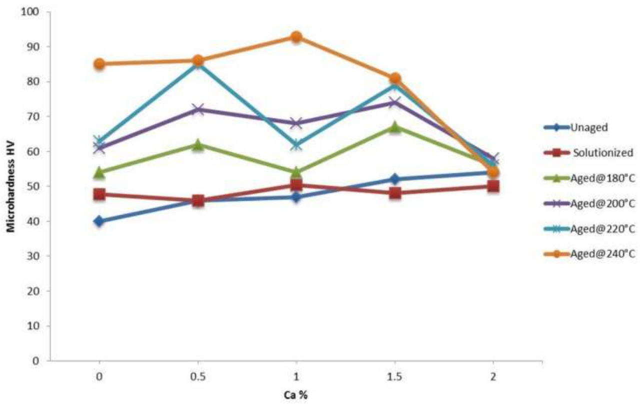


Figure 8: Microhardness Graph: Effect of Ca Composition vs. Aging Temperature

3.4. Immersion Test Results

The immersion test was carried out for the specimens in table 1 in 3.5% NaCl solutions, and the corrosion rate in terms of weight loss was provided in table 2. The results show that, AZ61+0.5%Ca aged at 200 °C shows the best corrosion resistance, than other stated conditions. The best result is due to presence of fine precipitates of sufficient Al_2Ca and discontinuity β phase (corrosive) in Mg matrix.

Table 2: Corrosion Rate of Exposed Samples

CORROSION RATE (mpy)					
% Ca	**Without Aging**	**180° C**	**200° C**	**220° C**	**240° C**
base	6048	5640	5423	7217	7021
0.50%	4079	3163	2659	6766	6521
1%	5804	4910	4767	5037	4886
1.50%	6607	6057	5417	5761	5883
2%	6933	6319	6191	6140	6377

3.5. SEM after Immersion

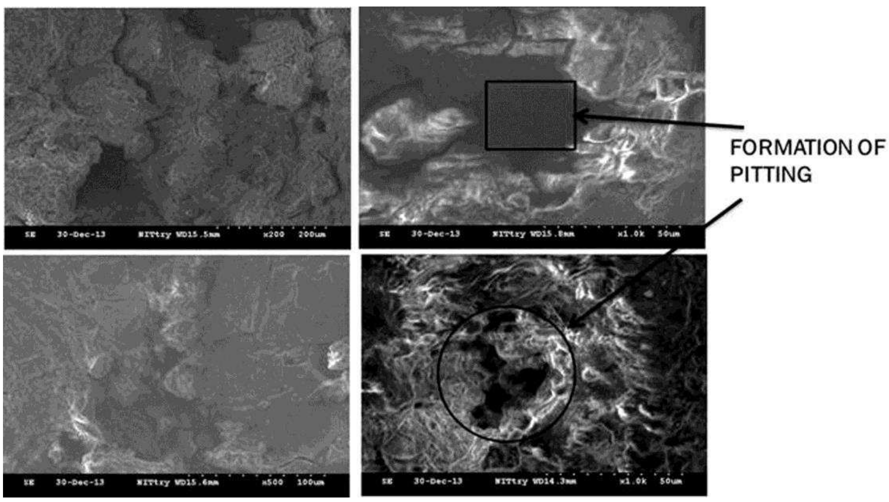


Figure 9: Aged Specimen after Immersion Test

CONCLUSIONS

- Ca addition to AZ61 magnesium alloy refines the cell size and the $Mg_{17}Al_{12}$ phase. With Ca addition, a new Al_2Ca phase is formed and the amount of the $Mg_{17}Al_{12}$ phase decreases. The Al_2Ca phase increases and is distributed along cell boundaries with increasing Ca content.
- The β -$Mg_{17}Al_{12}$ phase was getting to distribute along the grain boundary discontinuously after treated at 420°C, ageing for 16 h followed by air-cooling. After Solution treatment, β-Phase did not completely dissolve into α -
- Mg phase. The residual β -$Mg_{17}Al_{12}$ phase distributed along the grain boundary and had block like or island shapes. The size of α -Mg was getting to be coarser while increasing the aging temperature.
- The refined microstructure results in the improvement of corrosion resistance on AZ61 magnesium alloy. Calcium added upto 1 wt% of the AZ61 alloy improves the corrosion resistance of the alloy
- Immersion test results shows that 0.5% Ca sample has better corrosion resistance than others.
- Increased aging temperature coarsens the α- Mg as revealed on the microstructure. Finally samples aged at 200°C possess higher corrosion resistance compared to samples aged at other temperatures.

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